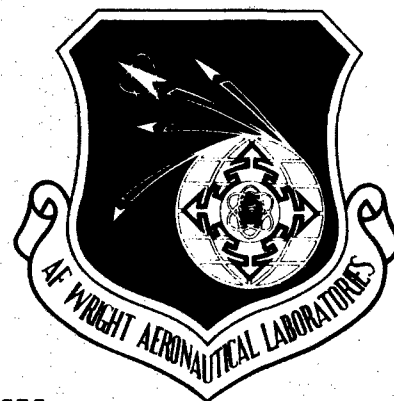AFWAL-TR-85-4040

ADA101859

ACETYLENE TERMINATED SULFONE RESIN PRECURSORS OF
TAILORED LENGTH VIA A MODIFIED ULLMANN ETHER SYNTHESIS

Marilyn R. Unroe
Frederick L. Hedberg, PhD

Polymer Branch
Nonmetallic Materials Division

May 1985

Final Report for Period April 1981 to August 1982

Approved for public release; distribution unlimited.

20040219263

MATERIALS LABORATORY
AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
AIR FORCE SYSTEMS COMMAND
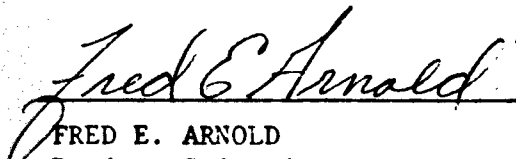WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

FRED E. ARNOLD
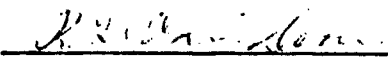Project Scientist

R. L. VAN DEUSEN
Chief, Polymer Branch

FOR THE COMMANDER

GEORGE E. HUSMAN, Chief
Nonmetallic Materials Division

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER AFWAL-TR-85-4040	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE *(and Subtitle)* ACETYLENE TERMINATED SULFONE RESIN PRECURSORS OF TAILORED LENGTH VIA A MODIFIED ULLMANN ETHER SYNTHESIS		5. TYPE OF REPORT & PERIOD COVERED Final Technical Report April 1981 to August 1982
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Marilyn R. Unroe Frederick L. Hedberg, PhD		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS Materials Laboratory (AFWAL/MLBP) Air Force Wright Aeronautical Laboratories Wright-Patterson Air Force Base, Ohio 45433		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 62102F/2419/04/24190415
11. CONTROLLING OFFICE NAME AND ADDRESS Materials Laboratory (AFWAL/MLBP) Air Force Wright Aeronautical Laboratories Wright-Patterson Air Force Base, Ohio 45433		12. REPORT DATE May 1985
		13. NUMBER OF PAGES 37
14. MONITORING AGENCY NAME & ADDRESS*(if different from Controlling Office)*		15. SECURITY CLASS. *(of this report)* Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT *(of this Report)*

Approved for public release; distribution unlimited

17. DISTRIBUTION STATEMENT *(of the abstract entered in Block 20, if different from Report)*

18. SUPPLEMENTARY NOTES

19. KEY WORDS *(Continue on reverse side if necessary and identify by block number)*

Acetylene terminated sulfone
Ullmann ether reaction
4,4'-bis(3-bromophenoxy)phenylsulfone
reactive oligomers

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

The Ullmann ether reaction of 4,4'-sulfonyl with 1,3-dibromobenzene was carried out in 2,4,6-collidine with cuprous oxide to afford high yields of a mixture of 4,4'-bis(3-bromophenoxy)phenylsulfone (BPDS) and its associated oligomers (OBPDS). This mixture is a low-cost precursor to the ATS composite resin system, formed by replacing the bromine atoms by terminal acetylene groups. The ratio of BPDS to OBPDS was found to be tailorable by varying stoichiometry, permitting selection of average ATS oligomer length for desired balances between processing and mechanical properties.

DD ₁ ᴶᴬᴺ ₇₃ FORM 1473   EDITION OF 1 NOV 65 IS OBSOLETE

FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project No. 2419, "Nonmetallic and Composite Materials," Task No. 241904, Work Unit Directive 24190415, "Structural Resins." It was administered under the direction of the Materials Laboratory, Air Force Wright Aeronautical Laboratories, Wright-Patterson Air Force Base, Ohio, with Dr. F. E. Arnold as the AFWAL/ML Work Unit Scientist. This report describes work conducted from April 1981 to August 1982.

The work described in this report was conducted by Dr. F. L. Hedberg and Marilyn R. Unroe of the Materials Laboratory. The manuscript was released by the authors in December 1982, for publication as a technical report.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

LIST OF TABLES

SECTION I

INTRODUCTION

A large variety of acetylene terminated (AT) resin systems have been prepared and studied in recent years (Reference 1). The properties of this family of addition-curing resins have indicated a high potential for structural composite applications in aerospace systems. The earliest AT resins were based upon imide or quinoxaline technology. Although these resins show 500°F (260°C) use temperature potential, they are currently rather expensive. For many structural composite applications, a 350°F (177°C) use temperature requirement is specified. The state-of-the-art resin used to meet this requirement is epoxy. Its major attribute is its combination of void-free addition cure, ease of processing, good mechanical properties, and low cost. It was discovered, however, that epoxy resins absorb moisture in high humidity environments, causing a deterioration in mechanical properties at elevated temperatures (275-300°F) (Reference 2).

Air Force sponsored research in recent years has been directed toward the discovery and development of new composite resins which would display all of the advantages of epoxy resins, but without the moisture sensitivity problem. One of the first resins to show such potential was the AT resin, 4,4'-bis(3-ethynylphenoxy)-phenylsulfone (ATS) (Reference 3). Its initial limitation, however, was very high cost. As a result of contractual research for the Air Force at Gulf Research and Development Company, a new, low cost synthesis approach to ATS was developed (References 4 and 5) as shown in Equation 1. The preparation utilized readily

2 Br—⟨benzene⟩—Br + 1 HO—⟨ ⟩—SO₂—⟨ ⟩—OH

1. Sulfolane/Toluene
   KOH, 120°C

2. CuCl, Pyridine
   170°C, 20h

Br—[⟨ ⟩—O—⟨ ⟩—SO₂—⟨ ⟩—O—⟨ ⟩]ₙ—Br   n=1 BPDS
                                          n>1 OBPDS

$$HC{\equiv}C{-}\underset{CH_3}{\overset{CH_3}{C}}{-}OH \qquad \emptyset_3P,\ (\emptyset_3P)_2PdCl_2,\ CuI \qquad Et_3N$$

$$HO{-}\underset{CH_3}{\overset{CH_3}{C}}{-}C{\equiv}C{-}[\ \ ]{-}O{-}[\ \ ]{-}SO_2{-}[\ \ ]{-}O{-}[\ \ ]{-}C{\equiv}C{-}\underset{CH_3}{\overset{CH_3}{C}}{-}OH$$

KOH | Toluene

HC≡C—[⟨ ⟩—O—⟨ ⟩—SO₂—⟨ ⟩—O—⟨ ⟩]ₙ—C≡CH   n=1 ATS
                                             n>1 OATS
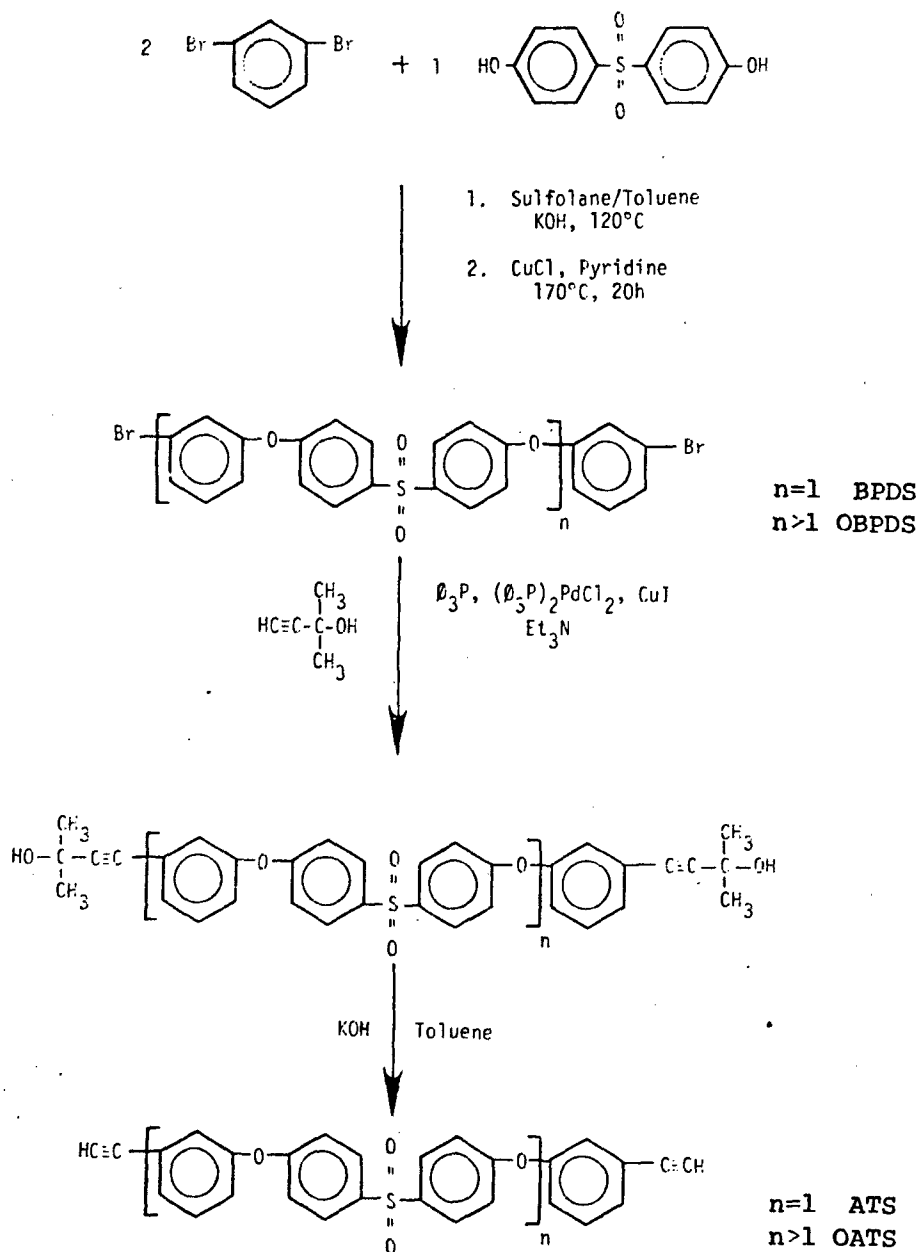
eq. (1)

available, inexpensive starting materials, 4,4'-sulfonyldiphenol and a mixture of

1,3-dibromobenzene (95%) and 1,4-dibromobenzene (5%), which were reacted together

in an Ullmann ether synthesis to form a mixture of 4,4'-bis(3-bromophenoxy)-

phenylsulfone (BPDS) and its oligomers (OBPDS). The BPDS-OBPDS mixture was then

converted, by replacement of the bromine atoms with terminal acetylene groups in

accordance with Equation 1, to a mixture of ATS and its corresponding oligomers

The critical step in the Gulf synthetic route was the BPDS/OBPDS synthesis, as the average oligomer length was established at this point. Oligomer length selection is necessary in order to obtain the desired balance between ease of processing, which is favored by shorter oligomers, mechanical properties, which are favored by longer oligomers, and ultimate use temperature after cure, which is favored by shorter oligomers. The conditions developed by Gulf for synthesizing the BPDS/OBPDS mixture consisted of reaction of 4,4'-sulfonyldiphenol with potassium hydroxide in sulfolane to form the bis-salt, followed by addition of the dibromobenzene mixture and cuprous chloride to effect the Ullmann ether condensation. The reaction under these conditions afforded BPDS/OBPDS mixtures, enabling this concept of ATS synthesis to be established. However, nonreproducible and incomplete conversions to BPDS/OBPDS were obtained, and no stoichiometric control of the BPDS/OBPDS ratio was achieved. It was the goal of this research to find a method of synthesis for BPDS/OBPDS mixtures which would afford (1): Reproducibly high yields, (2): Stoichiometric control of the BPDS/OBPDS ratio, and (3): A general route to BPDS/OBPDS analogues based upon other available bis-phenols. A valuable aid to this effort was the comprehensive review of the Ullmann reaction by Moroz and Shvartsberg (Reference 6).

RESULTS AND DISCUSSION

Initially a series of Ullmann ether condensations between 4,4'-sulfonyldiphenol (SDP) and 1,3-dibromobenzene (DBB) were performed in which the effects of base, copper catalyst, the absence or presence of a phase transfer catalyst (PTC) and a co-solvent on the formation of (BPDS) and its oligomers (OBPDS) were studied. Some of the reactions involved the _in situ_ generation of the dipotassium salt of SDP, while the remaining reactions maintained the free diphenol (SDP) as the reactant. Potassium carbonate was used instead of sodium carbonate since sodium cations were found to promote the formation of the monosubstituted salt (Reference 4). A molar excess (20:1 to 33:1) of DBB:SDP was maintained. Results of the thin layer chromatographic (TLC) analysis were noted as positive (+) for the presence of and negative (-) for the absence of BPDS, OBPDS, and the intermediate reaction product, 4-(3-bromophenoxy)-4'-hydroxydiphenylsulfone (Equation 2).

$$\text{(2)}$$
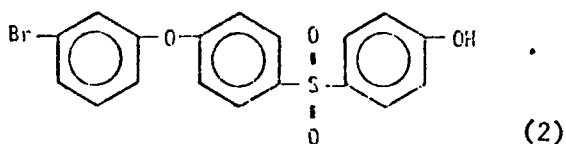
From the data of Table 1, which is a summary of the experimental conditions, BPDS and OBPDS are formed when either cetyltrimethylammonium bromide (CTAB) or benzyltriethylammonium chloride (BTAC) is used with cupric or cuprous chloride. The use of the free phenol or the dipotassium salt of the phenol as a reactant is not critical to the formation of BPDS and OBPDS since the products are formed in both types of reactions (Experimental, Runs #140, #143, #144, #146). Moreover, when 2,6-lutidine was used as a basic solvent in the presence of BTAC and Cu^{+1}, BPDS was generated (#144). In contrast, no BPDS was formed when BTAC was absent and Cu^{+2} was the catalyst present (#141).

TABLE 1

Summary of the Variation of Experimental Conditions for the
Ullmann Ether Synthesis Using SDP

Run	DBB:SDP mol ratio	Base	Co-solvent	PTC	Catalyst	Temp (°C)	Time h	BPDS, OBPDS	(A)
140	20:1	K_2CO_3		BTAC[a]	$CuCl_2$	150	44	+	-
141	31:1	2,6-lutidine			$CuCl_2$	160	24	-	-
143	33:1	K_2CO_3		BTAC	CuCl	170	69	+	+
144	33:1	2,6-lutidine		BTAC	CuCl	170	42	+	+
146	33:1	K_2CO_3		CTAB[b]	CuCl	170	92	+	+
147	33:1	2,4,6-collidine		CTAB	CuCl	170	69	-	+
148	33:1	2,4,6-collidine		CTAB	CuCl	170	91	-	+
149	33:1	K_2CO_3	$C_2H_6O_2$	CTAB	$CuCl/CuCl_2$	170	63	-	+
151	33:1	K_2CO_3		CTAB	CuCl	170	66	-	+
152	33:1	K_2CO_3	$C_2H_6O_2$	CTAB	CuCl	170	41	-	+
153	33:1	K_2CO_3/Na_2SO_4	$C_2H_6O_2$	CTAB	CuCl	170	67	-	+
154	33:1	2,4,6-collidine			Cu_2O	170	65	+	+

[a] Benzyltriethylammonium chloride
[b] Cetyltrimethylammonium bromide

Finally, BPDS or OBPDS was generated only once when CTAB was present in the reaction (#146). Although these same reaction conditions were repeated in #151, it appears that the detection of BPDS formation in #146 and #151 was a function of time.

Two sets of reactions are of particular note. First of all, no BPDS or OBPDS was formed when the PTC, Cu^{+1}, and 2,4,6-collidine were present in the reactions even with extended reaction time (Table 1, #147, #148). Second, in the reactions involving ethylene glycol as the co-solvent and excess solid bases to absorb any water generated during the reaction (Table 1, #149, #152, #153), BPDS was not formed and only compound (Equation 2) was formed.

Although the variety of specific conditions under which the Ullmann ether synthesis was attempted is a large source of discussion in itself, the ultimate drawback of all of the trials using PTCs is the presence or potential presence of products derived from reaction of SDP with the PTC, that is, 4-benzyloxy-4'-(3-bromophenoxy)diphenylsulfone (Equation 3) or 4-(3-bromophenoxy)-4'-methoxydiphenylsulfone (Equation 4). Both (Equation 3) and (Equation 4) exhibit similar TLC behavior with R_f values between BPDS and OBPDS dimer. The substituted products are formed by the substitution of functional groups

$$(3)$$

$$(4)$$

6
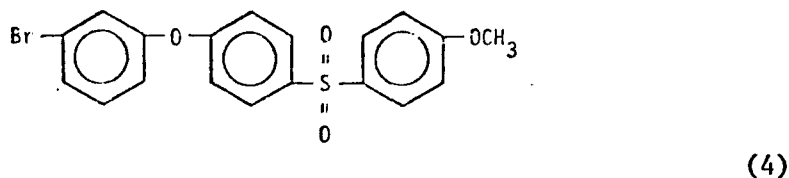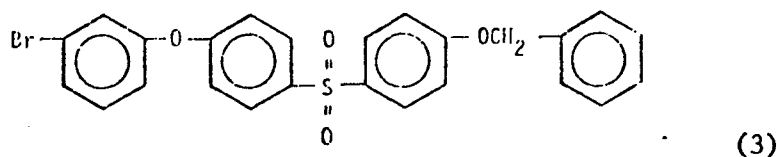
from the PTCs for the phenolic proton. The benzyl-substituted product was initially characterized by ^{1}H NMR (Figure 1), which integrated to an aromatic/methylenic ratio of 8.3:1 (8.5:1 theoretical), and by mass spectrum which indicated m/z values indicative of halogen monosubstitution and fragmentation (Experimental, Run #143). This sample was then used as a reference standard for TLC in subsequent reactions using BTAC.

The methoxy-substituted product (Equation 4) was initially characterized by ^{1}HNMR (Figure 2), which integrated to an aromatic/methyl ratio of 4:1 (4:1 theoretical), and by typical mass spectra values (Experimental, Run #151). The sample of (Equation 4) was also used as a reference standard for subsequent reactions using CTAB. However, Table 1 shows that the other reactions using CTAB did not form any BPDS; therefore, the standard of (Equation 4) was not needed.

The mass spectrum of what was assumed to be BPDS in #151 did not coincide with the mass spectrum of BPDS in #143 which was used as a TLC standard for all Ullmann reactions using SDP. Although this impurity was located at a similar R_f value as the BPDS standard, its molecular weight by the mass spectrum was 390 (MW BPDS: 560), its structure was not elucidated, and no BPDS appeared to be present (Table 1, #151).

The final trial reaction which was attempted was the reaction of DBB/SDP using 2,4,6-collidine and an amount of cuprous oxide that was equimolar to the SDP (Experimental, #154). No PTC was present in this trial. As the reaction proceeded, it was noticed that the speed at which BPDS and (Equation 2) were forming was quicker than in the preceding reactions. Although the final yield was low (15%), the amount of product was significantly higher than the yields obtained from some of the runs using PTCs (3-5%).

Further experimentation on the preparation of BPDS/OBPDS using cuprous oxide and 2,4,6-collidine concluded that the maximum yields of BPDS/OBPDS were obtained using a 2:1 equivalent excess of cuprous oxide:SDP. The amount
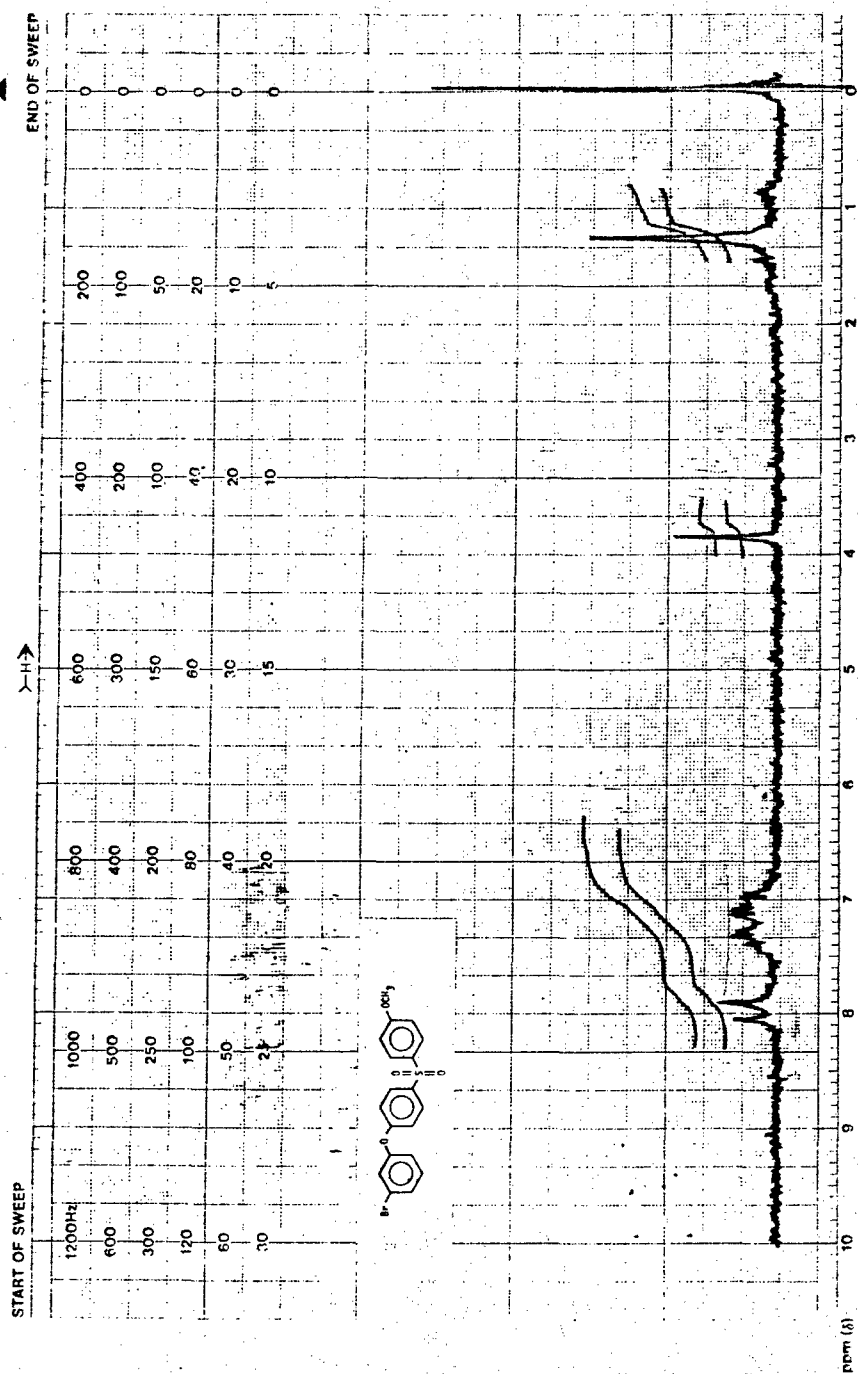
7

FIGURE 1. ^{1}H NMR Spectrum of 4-Benzyloxy-4'-(3-bromophenoxy)diphenylsulfone. (Equation 2).

FIGURE 2. ^{1}H NMR Spectrum of 4-(3-Bromophenoxy)-4''-methoxydiphenylsulfone. (Equation 4).

9

of collidine used was variable based on the total liquid available in the solution. In addition, a standard work-up was established using carbon tetrachloride to isolate the bulk of the solid impurities while liberating the product, warm HCl to dissolve any copper solids not captured in the filtration through Kieselguhr, and 10% aqueous KOH to extract any compound (Equation 2).

Table 2 is a summary of the initial reaction conditions for the preparation of BPDS/OBPDS, while Table 3 summarizes the results of the gravimetric determinations of the amounts of BPDS and dimeric and trimeric OBPDS obtained from column chromatography. The "trimer" fraction also contains all of the remaining higher oligomers. Table 3 also includes the total amount of (Equation 2) recovered, the copper content of the crude products, the total yield and monomer/oligomer ratio of each preparation.

Total yield is calculated for the BPDS/OBPDS since a calculation of yield based on the theoretical yield of monomer alone is meaningless. Other desired products, the OBPDS, are produced in the Ullmann ether synthesis, and they, too, must be accounted for since two or more moles of SDP are consumed per mole of OBPDS produced.

The calculation of a total yield includes the oligomeric products through the intermediate calculation of the "mole fraction". The "mole fraction" is a value which adjusts the moles of product (monomeric or oligomeric) produced against the moles of diphenol used initially.

From the data of Table 3, it is observed that total yield decreases as the DBB:SDP ratio decreases. One explanation for this observation is that the copper salt of the diphenol has difficulty finding a proximal DBB with which to react. Based on the information known about the Ullmann ether synthesis, the possibility of the copper salt finding a DBB molecule is further reduced by debromination of the aryl halogen at elevated temperatures (Reference 7). Some debromination was evident in the mass spectrum of BPDS (Experimental, General Preparation of BPDS/OBPDS).

10

TABLE 2

Reaction Conditions for the Preparation of BPDS/OBPDS

Reaction No.	Wt. DBB[a] g(mmol)	Wt. SDP g(mmol)	Wt. Cu2O g(mmol)	Wt. Collidine g(mmol)	DBB:SDP mol ratio	Time h
155	124.70(528)	4.00(16)	4.78(33)	12.10(100)	33:1	45
183	124.70(528)	4.00(16)	4.78(33)	12.10(100)	33:1	72
158	74.01(320)	4.00(16)	4.78(33)	12.10(100)	20:1	22
160	74.01(320)	4.00(16)	4.78(33)	12.10(100)	20:1	72
186	56.64(240)	4.00(16)	4.61(32)	12.10(100)	15:1	26
161	37.76(160)	4.00(16)	4.61(32)	12.10(100)	10:1	41
164	188.80(800)	20.00(80)	23.04(160)	48.40(400)	10:1	42
162	30.20(128)	4.00(16)	4.61(32)	12.10(100)	8:1	26.5
156	22.70(96)	4.00(16)	4.78(33)	12.10(100)	6:1	21
169	22.70(96)	4.00(16)	4.61(32)	12.10(100)	6:1	21
163	15.10(64)	4.00(16)	4.61(32)	24.20(200)	4:1	41
165	7.55(32)	4.00(16)	4.61(32)	24.20(200)	2:1	42
167	7.55(32)	4.00(16)	4.61(32)	24.20(200)	2:1	120
166	5.66(24)	4.00(16)	4.61(32)	24.20(200)	1.5:1	26

[a]Aldrich meta-dibromobenzene (97%)

11

TABLE 3

Results of the Preparation of BPDS/OBPDS

Reaction No.	DBB:SDP	Crude Yield g	Monomer g	Dimer g	Trimer g	Mole Fraction Monomer	Dimer	Trimer	Total Yield %	BATS:OBATS wt. ratio	(A)	
155	33:1	8.41	6.58	0.55	0.11	0.01175	0.00124	0.00027	82.89	91:9	0.10	*
193	33:1	8.86	6.99	0.51	negl.	0.01268	0.00115	0.00000	85.19	93:7	0.05	12
158	20:1	6.38	5.10	0.51	negl.	0.00911	0.00115	0.00000	64.13	91:9	0.85	13
160	20:1	8.75	6.86	0.86	0.17	0.01230	0.00195	0.00042	91.7	87:13	0.10	15
186	15:1	8.82	6.57	1.04	negl.	0.01173	0.00235	0.00000	88.02	87:13	negl.	7
161	10:1	7.91	5.54	1.38	0.40	0.00989	0.00312	0.00099	87.52	75:25	negl.	3
164	10:1	37.47	26.98	8.24	1.12	0.04810	0.01860	0.00279	86.87	75:25	0.09	12
162	8:1	5.49	3.34	0.86	0.22	0.00596	0.00195	0.00055	52.85	75:25	*	2
196	6:1	8.58	4.26	1.37	0.43	0.00761	0.00310	0.00107	73.63	70:30	0.10	*
169	6:1	6.43	4.44	1.52	0.35	0.00790	0.00360	0.00090	77.31	70:30	negl.	5
163	4:1	5.83	2.64	1.32	0.22	0.00471	0.00299	0.00055	51.54	63:37	0.17	8
165	2:1	2.60	0.94	0.73	0.21	0.00168	0.00165	0.00052	24.07	50:50	0.22	5
167	2:1	1.88	0.52	0.48	0.32	0.00093	0.00114	0.00080	17.91	40:60	negl.	5
166	1.5:1	1.13	0.28	0.28	0.20	0.00050	0.00066	0.00050	10.36	37:63	0.02	6

*Data not available

In addition, as the DBB:SDP decreases, the amount of monomer decreases as evidenced by the yield of monomer (g) and the BPDS/OBPDS ratio. Again, at lower DBB:SDP ratios, the copper salt of the phenol has difficulty finding a DBB molecule with which to react. At lower DBB:SDP ratios the amount of DBB has become a nearly limiting factor, and the copper salt of SDP is more likely to find a molecule of BPDS with which to react, thus increasing the amount of oligomer formed.

When reaction times are similar, the reproducibility of the total yield and monomer/oligomer ratio are consistent for each DBB:SDP ratio. For example, even though reaction #164 is a scaled-up version of reaction #161, the reaction times were nearly the same (Table 2), the total yield differs only by 0.65%, and the monomer/oligomer ratio is the same (Table 3). Two other examples of the good reproducibility of the reaction are at the DBB:SDP ratios of 33:1 and 6:1 (Tables 2 and 3).

When the total yield vs. the DBB:SDP ratio is plotted (Figure 3), a curve develops which is linear at lower DBB:SDP ratios and flattens to a near maximum conversion at 20:1 DBB:SDP. This curve reinforces the idea that at the higher DBB:SDP ratios, total conversion reaches a maximum, while at lower DBB:SDP ratios conversion to BPDS and OBPDS is inefficient due to the paucity of available reactants, solvent effects, the nonreactivity of SDP which may cause decomposition in time and an increase in the side reactions, or the solubility of the copper complexes of the oligomers.
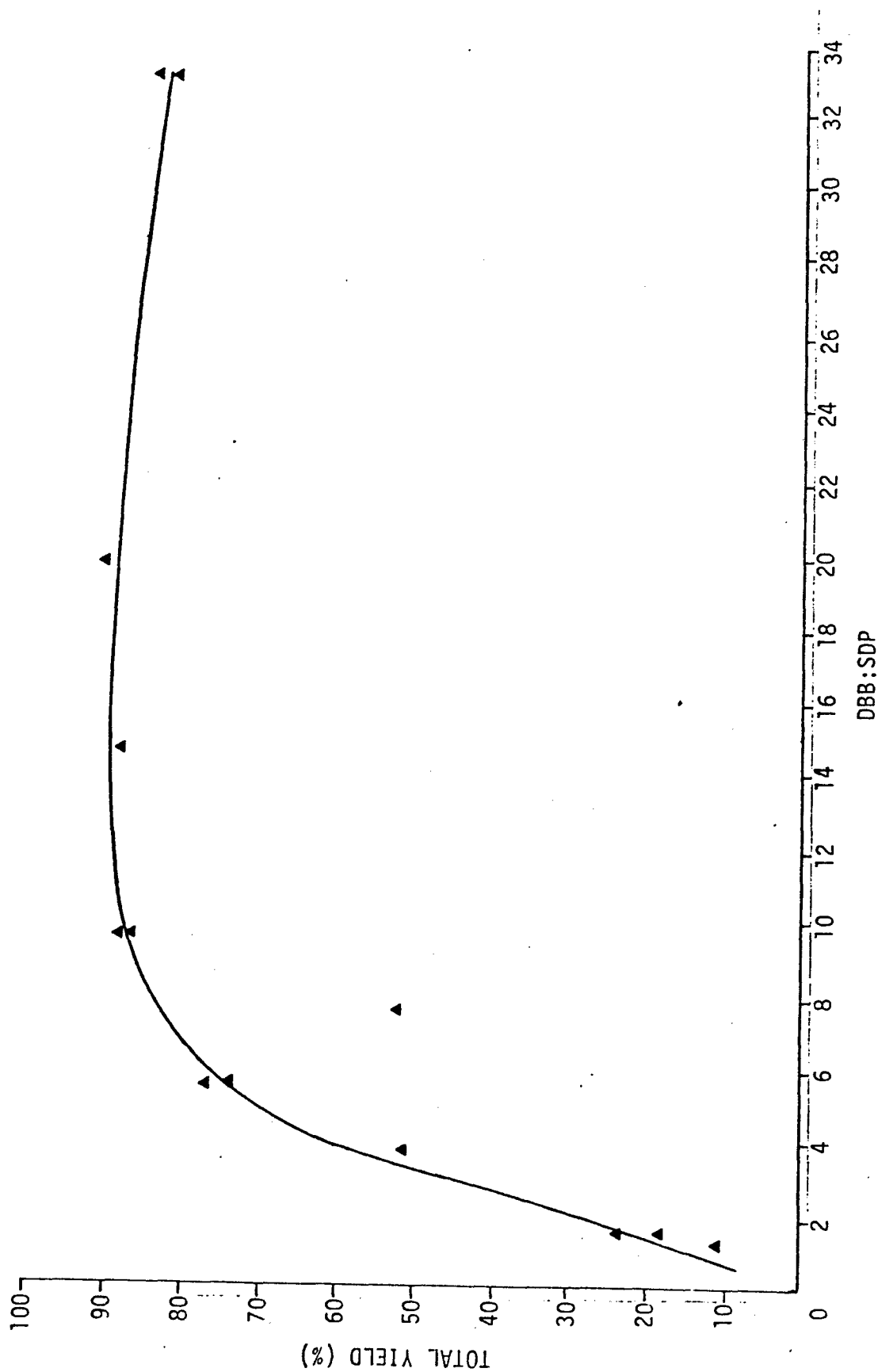
FIGURE 3. Total Yield vs. DBB:SDP (Table 3) for Preparation of BPDS/OBPDS.

SECTION III

CONCLUSIONS

The new preparative method for BPDS/OBPDS described in this report provides a convenient route to ATS resin systems with tailored average molecular weight. Tthe only limitation appears to be the substantial drop in yield for OBPDS contents higher than 50%. A further advantage of the preparative method is its generalness. It has been found to be applicable to the reaction of 1,3-dibromobenzene or 1,4-dibromobenzene both with other low-cost bis-phenols such as resorcinol, bis-phenol A and 4,4'-thiodiphenol to synthesize the brominated precursors of other AT systems, as well as with mono-phenols such as 3-phenoxyphenol to synthesize precursors to monofunctional AT compounds used as reactive diluents (Reference 8). An investigation is currently underway to determine the amenability of the new preparative method to scale-up.

SECTION IV

EXPERIMENTAL

Reagents

Deuterochloroform (99.6% gold label), 4,4'-sulfonyldiphenol (98%) (SDP), 2,4,6-collidine, 2,6-lutidine, benzyltriethylammonium chloride (BTAC), cetyltrimethylammonium bromide (CTAB), and cuprous oxide (96.4%) were purchased from Aldrich Chemical Company. The 1,3-dibromobenzene (DBB) used was purchased from either Aldrich Chemical Company (97%) or Eastman Kodak Company (purity unknown). The bisphenol A (BPA) was purchased from Eastman Kodak Company. Cuprous chloride (97%) and magnesium sulfate (anhydrous) were purchased from Fisher Scientific Company. Cupric chloride (reagent), potassium carbonate (reagent, anhydrous), kieselguhr, and ethylene glycol (99%) were purchased from Matheson, Coleman, and Bell. Silica gel (Woelm DCC) was purchased from ICN Nutritional Biochemicals. Thin layer chromatography (TLC) strips made of silica gel with UV-254 indicator were purchased from Brinkman Instruments Inc. All solvents and inorganic acids and bases used were reagent grade. All starting materials, catalysts, organic and inorganic reagents were utilized without additional purification.

Instrumentation

Infrared (IR) spectra were performed with a Beckman Model IR-33 spectrometer using potassium bromide (KBr) films at concentrations of 2% by weight. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Varian EM-360A spectrometer using 10% weight/volume solutions in deuterochloroform ($CDCl_3$) with tetramethylsilane as an internal standard.

16

Melting points were obtained using a Mel-Temp capillary melting point

apparatus. Elemental analyses and emission spectra were performed by

the Analytical Branch of the Air Force Wright Aeronautical Laboratories,

Wright-Patterson Air Force Base, Dayton, Ohio. Chemical ionization mass

spectra (CIMS), which were also done by the Air Force Wright Aeronautical

Laboratories, were performed on either a Finnegan 4021 GC/MS/DS or a

DuPont 21-490 mass spectrometer using a methane purge.

Reaction of DBB, SDP, K_2CO_3, $CuCl_2$ and BTAC (Run #140)

To a dry 25 ml three-necked roundbottom flask fitted with reflux

condenser, nitrogen purge, and thermometer was added DBB (5.66 g, 24 mmol).

The solvent was stirred at room temperature under nitrogen before SDP

(1.00 g, 4 mmol), cupric chloride (0.05 g, 0.4 mmol), and potassium

carbonate (1.66 g, 12 mmol) were added to the flask. No detectable

exotherm was noted with the addition of base to the opaque peach solution.

The flask was heated by oil bath to an internal temperature of 150°C

under a nitrogen atmosphere until TLC (2:1 CH_2Cl_2:Hexane) showed the

formation of BPDS or 4-(3-bromophenoxy)-4'hydroxydiphenylsulfone (Equation 2).

At 22 h BTAC (0.09 g, 0.4 mmol) was added to the reaction. At 29 h TLC

indicated the formation of BPDS in the reaction. However, at 44 h there

was no appreciable increase in BPDS by TLC and the presence of compound

(Equation 2) was not determined.

Reaction of DBB, SDP, K_2CO_3, CuCl and BTAC (Run #143)

To a 25 ml three-necked roundbottom flask fitted with reflux condenser,

nitrogen purge, and thermometer was added DBB (15.60 g, 66 mmol). The solvent

was stirred at room temperature under a nitrogen atmosphere before the

17

addition of SDP (0.50 g, 2 mmol), potassium carbonate (0.83 g, 6 mmol), cuprous chloride (0.02 g, 0.2 mmol), and BTAC (0.06 g, 0.3 mmol). The clear peach solution with undissolved K_2CO_3 was heated to an internal temperature of 170°C under nitrogen until TLC (CH_2Cl_2) on a silica strip, which was developed two times after activating the strip in a 100°C convection oven for one minute, had shown the absence of SDP and the formation of BPDS. By 69 h a substantial amount of BPDS was formed along with a comparable amount of an impurity [compound (Equation 3)] which occurred immediately below BPDS on TLC. The DBB was distilled off at reduced pressure and the residue was extracted with methylene chloride (2x15 ml). The extract was poured into refluxing pentane (150 ml). The pentane was decanted from the oily residue and evaporated to dryness. The residue from the pentane decantate was chromatographed on a silica column using carbon tetrachloride to remove residual DBB and methylene chloride to remove the BPDS and compound (Equation 3) as separate bands. The BPDS and compound (Equation 3) residues were dried in a 40°C oven for 2 h under reduced pressure. Analysis of 4-benzyloxy-4'-(3-bromophenoxy) diphenylsulfone [compound (Equation 3)]: mp 122-125°C; ^{1}H NMR δ6.7-8.1 (m, aromatic, 17 H), 5.11 (s, methylene, 2 H) (Figure 1); mass spectrum, m/z (relative intensity) 497 (100, M+1, ^{81}Br), 496 (71, M, ^{81}Br), 495 (100, M+1, ^{79}Br), 494 (25, M, ^{79}Br), 435 (19, ^{81}Br), 433 (19, ^{79}Br), 247 (+SO$_2$ArOCH$_2$Ar, 30). Analysis of BPDS: ^{1}H NMR δ6.7-8.1 (m, aromatic, 12 H); mass spectrum, m/z (relative intensity) 563 (17, M+1, ^{81}Br), 562 (58, M, ^{81}Br), 561 (48, M+1, ^{81}Br ^{79}Br), 560 (100, M, ^{81}Br ^{79}Br), 559 (47, M+1, ^{79}Br), 558 (55, M, ^{79}Br), 313 (22, M-ArOArBr, ^{81}Br), 311 (24, M-ArOArBr, ^{79}Br).

Reaction of DBB, SDP, K_2CO_3, CuCl and CTAB (Run #146)

To a 25 ml three-necked roundbottom flask fitted with reflux condenser, nitrogen purge, and thermometer were added DBB (15.60 g, 66 mmol) and SDP (0.50 g, 2 mmol). The solution was stirred under a nitrogen atmosphere at room temperature until the SDP was suspended. The following reagents were then added: potassium carbonate (0.83 g, 6 mmol), CTAB (0.07 g, 0.2 mmol), and cuprous chloride (0.02 g, 0.2 mmol). No exotherm was noted with the addition of base or catalyst. The flask was heated under a nitrogen atmosphere to an internal temperature of 170°C until TLC (CH_2Cl_2 (Experimental, Run #143) indicated the presence of BPDS or (Equation 2). Only (Equation 2) was present by TLC at 24 h. By 92 h BPDS, OBPDS, (Equation 2), and a cleavage product with a similar R_f value as (Equation 3) (Experimental, Run #143) were formed.

Reaction of DBB, SDP, K_2CO_3, CuCl, $CuCl_2$, CTAB and Ethylene Glycol (Run #149)

To a 100 ml three-necked roundbottom flask fitted with reflux condenser, nitrogen inlet, and thermometer were added ethylene glycol (22.40 g, 361 mmol), potassium carbonate (1.66 g, 12 mmol), and SDP (1.00 g, 4 mmol). The solution was stirred under a nitrogen atmosphere at room temperature until the solids dissolved. To the clear pale peach solution were added DBB (31.20 g, 132 mmol), cuprous chloride (0.04 g, 0.4 mmol) and CTAB (0.14 g, 0.4 mmol). When the CTAB was added the two phase system was homogenized and the solution was changed to an opaque pastel yellow. The flask was heated to 170°C under nitrogen until TLC on a silica strip (activated in a 100°C oven for one minute and then developed first in ethyl ether and then in methylene chloride) indicated the presence of BPDS. At 16 h only a slight amount

19

of (Equation 2) was present. At 25 h enough cuprous chloride was added to make a total of 0.12 g (1.2 mmol) added to the reaction. TLC at 40 h showed that no BPDS had formed. Enough cupric chloride (0.16 g, 1.2 mmol) was added at 40.5 h to equal the molar amount of cuprous chloride. No BPDS was formed by 63 h; only (Equation 2) was present by TLC.

Reaction of DBB, SDP, K_2CO_3, CuCl, and CTAB (Run #151)

To a 50 ml three-necked roundbottom flask fitted with reflux condenser, nitrogen inlet, and thermometer was added DBB (31.20 g, 132 mmol). The reactant was purged under a nitrogen atmosphere at room temperature before the addition of SDP (1.00 g, 4 mmol) and potassium carbonate (3.31 g, 24 mmol). The solution was stirred for an additional five minutes before cuprous chloride (0.04 g, 0.4 mmol) and CTAB (0.15 g, 0.4 mmol) were added. The flask was heated to an internal temperature of 170°C until TLC (CH_2Cl_2) (Experimental, Run #143) indicated the presence of BPDS. By 66 h BPDS, OBPDS, (Equation 2), and a suspected cleavage product, 4-(3-bromophenoxy)-4'-methoxydiphenylsulfone (Equation 4) had formed. The reaction was poured into water (150 ml) and a thick dark beige solution was formed. The solution was extracted with methylene chloride (4x50 ml). The methylene chloride was washed with water (2x125 ml) and stripped to dryness by rotary evaporation to yield 0.92 g crude product. The crude product was chromatographed on silica gel (490 g) with carbon tetrachloride to remove DBB. The BPDS was stripped from the column with 4:1 methylene chloride: carbon tetrachloride. The suspected cleavage product and OBPDS were removed as separate bands with methylene chloride. Analysis of (Equation 4): ^{1}H NMR δ6.75-8.1 (m, aromatic, 12 H), 3.85 (s, methyl, 3 H),

20

1.25 (s) (Figure 2); mass spectrum, m/z (relative intensity) 421 (100, M+1, ^{81}Br), 420 (63, M, ^{81}Br), 419 (86, M+1, ^{79}Br), 418 (46, M, ^{79}Br), 171 (+SO$_2$ArOCH$_3$, 30). Analysis of unknown impurity of MW 390: mass spectrum, m/z (relative intensity) 391 (100, M+1), 313 (77, M-Ar), 279 (36), 205 (49), 149 (61), 91 (53).

Reaction of DBB, SDP, K$_2$CO$_3$, CuCl, CTAB and Ethylene Glycol (Run #152)

To a 100 ml three-necked roundbottom flask fitted with a nitrogen inlet and a fractionating column were added SDP (1.00 g, 4 mmol), and ethylene glycol (22.40 g, 361 mmol). The solution was stirred at room temperature under a nitrogen atmosphere for five minutes before the addition of potassium carbonate (3.32 g, 24 mmol), CTAB (0.15 g, 0.4 mmol) and toluene (15 ml). The flask was heated to 85°C under the inert atmosphere to distill the water/toluene azeotrope. The flask was refilled with toluene (2x15 ml) and cooled to 30°-40°C after the last distillation. At this temperature DBB (31.20 g, 132 mmol) and cuprous chloride (0.04 g, 0.4 mmol) were added to the flask. The fractionation column was replaced by a reflux condenser, and the flask was heated to 170°C until TLC (CH$_2$Cl$_2$) indicated the presence of BPDS. Only (Equation 2) was present by TLC at 17 h. At 18.5 h molecular sieves (Linde 5A, 200 g) were added to absorb any water present. No BPDS was formed by TLC at 22 h. An additional amount of cuprous chloride (0.04 g, 0.4 mmol) was added at 24 h. No BPDS was formed by 41 h based on TLC.

Reaction of DBB, SDP, K_2CO_3, CuCl, CTAB and Ethylene Glycol (Run #153)

To a 100 ml three-necked roundbottom flask fitted with reflux condenser, nitrogen inlet, and thermometer were added ethylene glycol (22.4 g, 361 mmol), potassium carbonate (3.32 g, 24 mmol), and anhydrous sodium sulfate (10.00 g, 70 mmol). The solution was stirred vigorously at room temperature under a nitrogen atmosphere for five minutes before the addition of SDP (1.00 g, 4 mmol). The solution again was stirred for 10 minutes before DBB (31.20 g, 132 mmol), CTAB (0.15 g, 0.4 mmol), and cuprous chloride (0.04 g, 0.4 mmol) were added to the flask. The flask was heated to 170°C under nitrogen until TLC on a silica strip, which was activated in a 100°C oven for one minute and developed first in methylene chloride and then in ethyl ether, indicated the presence of BPDS or (Equation 2). A slight amount of (Equation 2) was present and no BPDS was formed by TLC at 67 h.

Reaction of DBB, SDP, 2,6-Lutidine and $CuCl_2$ (Run #141)

To a 50 ml three-necked roundbottom flask fitted with reflux condenser, nitrogen inlet, and thermometer was added DBB (29.25 g, 124 mmol). The reactant was stirred under a nitrogen atmosphere at room temperature before the addition of 2,6-lutidine (9.42 g, 88 mmol). This solution was also stirred for 10 minutes under nitrogen at room temperature before the addition of SDP (1.00 g, 4 mmol) and cupric chloride (0.05 g, 0.4 mmol). The flask was heated to an internal temperature of 160°C. The solution darkened to a deep oxblood color upon heating. No BPDS or (Equation 2) was present in the reaction after 20.5 h by TLC analysis. After 3 h additional reflux at 170°C, no BPDS or (Equation 2) was formed.

Reaction of DBB, SDP, 2,6-Lutidine, CuCl and BTAC (Run #144)

To a dry 25 ml three-necked roundbottom flask fitted with reflux condenser, nitrogen inlet, and thermometer were added DBB (15.60 g, 66 mmol) and 2,6-lutidine (0.64 g, 6 mmol). The solution was stirred for 10 minutes under a nitrogen purge before the addition of SDP (0.50 g, 2 mmol), BTAC (0.06 g, 0.3 mmol), and cuprous chloride (0.02 g, 0.2 mmol). The flask was heated to an internal temperature of 170°C under nitrogen until TLC (CH_2Cl_2) indicated the formation of BPDS and (Equation 2). By 18 h (Equation 2) was formed; by 42 h BPDS, OBPDS, and the cleavage product (Equation 3) was formed.

Reaction of DBB, SDP, 2,4,6-Collidine, CuCl, and CTAB (Run #147)

To a 25 ml three-necked roundbottom flask fitted with reflux condenser, nitrogen inlet, and thermometer were added DBB (15.60 g, 66 mmol) and 2,4,6-collidine (0.73, 6 mmol). The solution was stirred under a nitrogen atmosphere at room temperature before the addition of SDP (0.50 g, 2 mmol) and cuprous chloride (0.02 g, 0.2 mmol). The flask was heated to an internal temperature of 170°C under nitrogen until the presence of BPDS or (Equation 2) was indicated by TLC. The following procedure was established for the TLC of the reaction: an aliquot (1-2 ml) of the reaction was quenched in 1:1 12 N HCl: water and the organic products were extracted with methylene chloride (5 ml); the organic layer was spotted on a silica strip, and the strip was activated in a 100°C oven for one minute before elution with methylene chloride. Since no reaction had occurred by 26 h, another quantity of cuprous chloride (0.02 g, 0.2 mmol) was added. Some (Equation 2) was formed by 42 h. CTAB (0.29 g, 0.8 mmol) was added to the reaction at 44 h. By 51 h more (Equation 2) was formed, but no BPDS was present after 69 h of reaction.

Reaction of DBB, SDP, 2,4,6-Collidine, CUCl, and CTAB (Run #148)

To a 25 ml three-necked roundbottom flask fitted with reflux condenser, nitrogen inlet, and thermometer were charged DBB (15.60 g, 66 mmol) and 2,4,6-collidine (0.73 g, 6 mmol). The solution was stirred under a nitrogen atmosphere at room temperature before the addition of SDP (0.50 g, 2 mmol), CTAB (0.07 g, 0.2 mmol), and cuprous chloride (0.02 g, 0.2 mmol). The flask was heated to an internal temperature of 170°C under nitrogen. At 19 h some (Equation 2) was detected by TLC analysis, but no BPDS was formed by 91 h.

Reaction of DBB, SDP, 2,4,6-Collidine and Cu_2O (Run #154)

To a 25 ml three-necked roundbottom flask fitted with a reflux condenser, nitrogen inlet, and thermometer were charged DBB (31.20 g, 132 mmol), and 2,4,6-collidine (1.45 g, 12 mmol). The solution was stirred at room temperature under a nitrogen atmosphere before the addition of SDP (1.00 g, 4 mmol) and cuprous oxide (0.06 g, 0.4 mmol). The flask was heated to 170°C under nitrogen until the presence of BPDS or (Equation 2) was indicated by TLC (CH_2Cl_2) on an activated silica strip (Experimental, Run #147). Although BPBS was formed as early as 16 h, very little was present after 24 h. Additional cuprous oxide (0.52 g, 3.6 mmol) was added to make an equimolar amount with SDP. More BPDS was formed by 40 h of reaction as indicated by TLC. After the reaction was stopped at 65 h, the flask residue was quenched in 10% sulfuric acid (100 ml) and extracted with methylene chloride (2x50 ml). The organic layer was washed with water and stripped to dryness by rotary evaporation. The residue was chromatographed on a silica column (5 cm dia. x 36 cm L) using carbon tetrachloride to remove the residual DBB. The BPDS/OBPDS was removed from the column with 4:1 carbon tetrachloride:methylene chloride, and (Equation 2) was stripped with 4:1 methylene chloride:ethyl ether.

24

A yield of 0.33 g (15%) BPDS was obtained after evaporation to dryness: mp 143–145°C; mass spectrum, m/z (relative intensity) 563 (78, M+1, ^{81}Br), 562 (67, M, ^{81}Br), 561 (100, M+1, ^{81}Br ^{79}Br), 560 (77, M, ^{81}Br ^{79}Br), 559 (76, M+1, ^{79}Br), 558 (32, M, ^{79}Br), 313 (30, M-ArOAr^{81}Br), 311 (27, M-ArOAr ^{79}Br); ^{1}H NMR δ6.9–8.1 (m, aromatic, 16 H).

General Preparation of BPDS/OBPDS Using Excess Cuprous Oxide and 2,4,6-Collidine

To an appropriate three-necked roundbottom flask fitted with reflux condenser, nitrogen inlet, and thermometer were added SDP (4.00 g, 16 mmol), cuprous oxide (4.61 g, 32 mmol), 2,4,6-collidine (12.1–24.2 g, 100–200 mmol) (Table 2), and a suitable quantity of DBB (Table 2). The solution was stirred under nitrogen at room temperature for 10 minutes before being heated to 170°C. As the temperature was increased, a series of color changes were observed: at room temperature the solution was a brilliant brick red; at 80°C the color was a dull brick red; by 150°C the solution was a deep magenta; at 170°C the solution was black. The flask was maintained at 170°C under a nitrogen atmosphere until the reaction was complete by TLC (CH_2Cl_2, 2:1 ethyl ether:hexane) (Experimental, Run #147). The collidine and remaining DBB were removed from the black residue by rotary evaporation under reduced pressure at 170°C. The residue was then dried for 4 h on the rotary evaporator under the same pressure and temperature conditions. The residue was dissolved in a minimal amount of methylene chloride and the solution was poured into carbon tetrachloride (250 ml). The mthylene chloride and 50 ml of carbon tetrachloride were distilled from the solution, the volume was refilled to 250 ml carbon tetrachloride, and 50 ml more of carbon tetrachloride was distilled from the solution. The solution was hot filtered through Kieselguhr (50 g) packed in a coarse porosity fritted Buchner funnel.

Most of the copper solids were captured in the frit while the filtrate was lightened to a clear brown solution. The filtrate was extracted by adding 12 N HCl (2x50 ml) at room temperature, heating the solution to 50°C for 0.5 h and separating. The HCl layers were green and the carbon tetrachloride was lightened to honey yellow. After washing with water (2x100 ml), the carbon tetrachloride was extracted with 10% aqueous potassium hydroxide (2x50 ml), separated, and washed with water (3x100 ml). After drying on magnesium sulfate (15.00 g), the carbon tetrachloride was removed by rotary evaporation at reduced pressure to yield the crude BPDS/OBPDS residue. A portion of the residue (ca. 0.50 g) was then chromatographed on a silica gel column (2 cm dia. x 25 cm L) using carbon tetrachloride to remove residual DBB, 2:1 carbon tetrachloride: methylene chloride to remove BPDS, 10:1 methylene chloride:carbon tetrachloride to remove OBPDS, and 2:1 methylene chloride:ethyl ether to remove residual (Equation 2). The fractions were dried by rotary evaporation and then dried in a 60-90°C oven at reduced pressure for 6 h. Analysis of BPDS: crystallized from CH_2Cl_2/Hexane (powder), mp 146-147°C; IR (film) 3100-3060, 1580 (aromatic), 1320 (SO_2), 1240 (ArOAr), 1150 cm^{-1} (SO_2) (Figure 4); ^1H NMR δ6.9-8.2 (m, aromatic, 16 H) (Figure 5); mass spectrum, m/z (relative intensity) 563 (81, M+1, ^{81}Br), 562 (69, M, ^{81}Br), 561 (100, M+1, ^{81}Br ^{79}Br), 560 (77, M, ^{81}Br ^{79}Br), 559 (81, M+1, ^{79}Br), 558 (31, M, ^{79}Br), 483 (30, M+1, ^{81}Br), 482 (20, M, ^{81}Br), 481 (31, M+1, ^{79}Br), 480 (12, M, ^{79}Br); Anal. Calc'd for $C_{24}H_{16}O_4SBr_2$: C, 51.43; H, 2.86; S, 5.71; Br, 28.54. Found: C, 51.58; H, 2.60; S, 5.73; Br, 28.57.

Analysis of the OBPDS dimer: oil; Anal. Calc'd for $C_{42}H_{28}O_8S_2Br_2$: C, 57.01; H, 3.17; S, 7.24; Br, 18.10. Found: C, 57.27; H, 2.92; S, 7.24; Br, 20.47.

Analysis of the OBPDS trimer: crystallized from CH_2Cl_2/hexane (powder), mp 98–104°C; Anal. Calc'd for $C_{60}H_{40}O_{12}S_3Br_2$: C, 59.60; H, 3.31, S, 7.96; Br, 13.23. Found: C, 59.85; H, 3.06; S, 8.01; Br, 13.36.
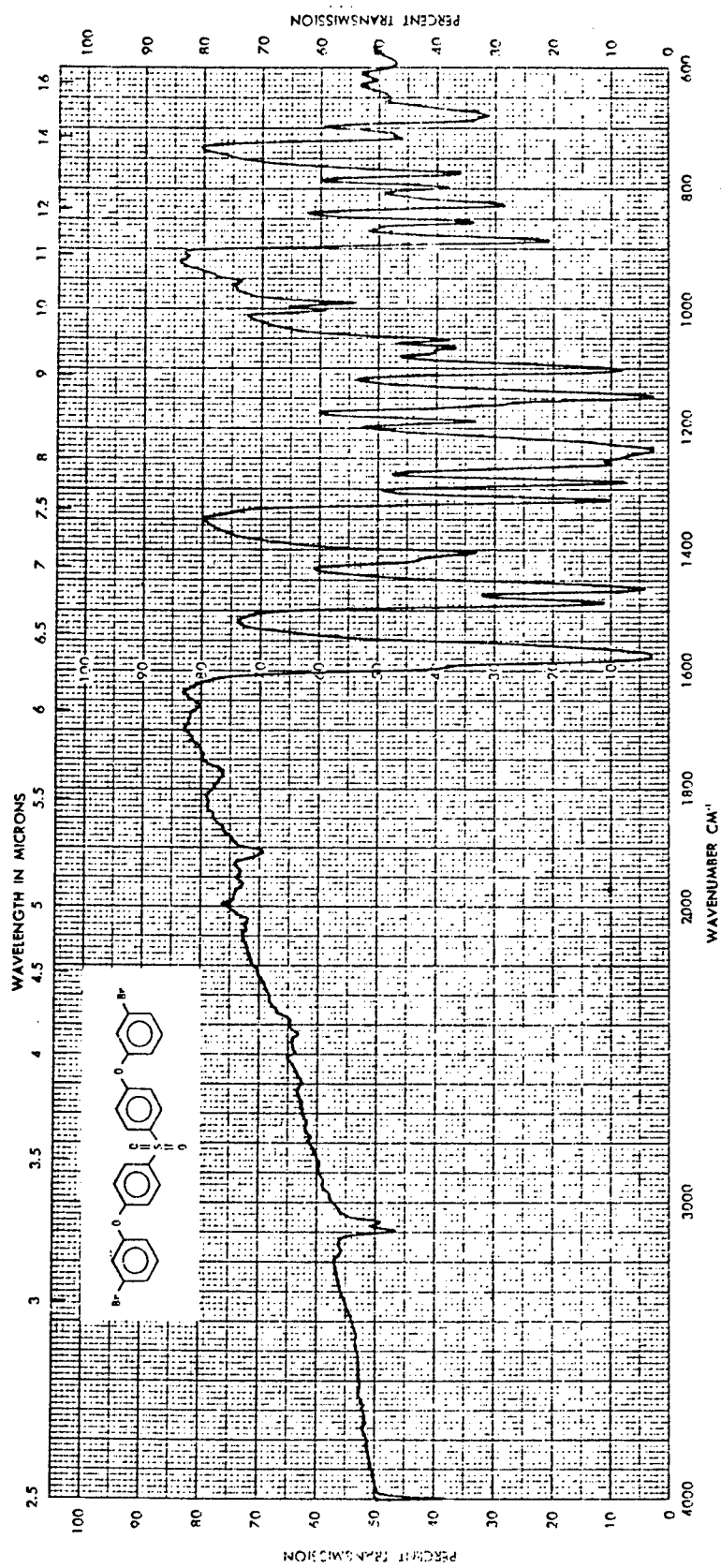
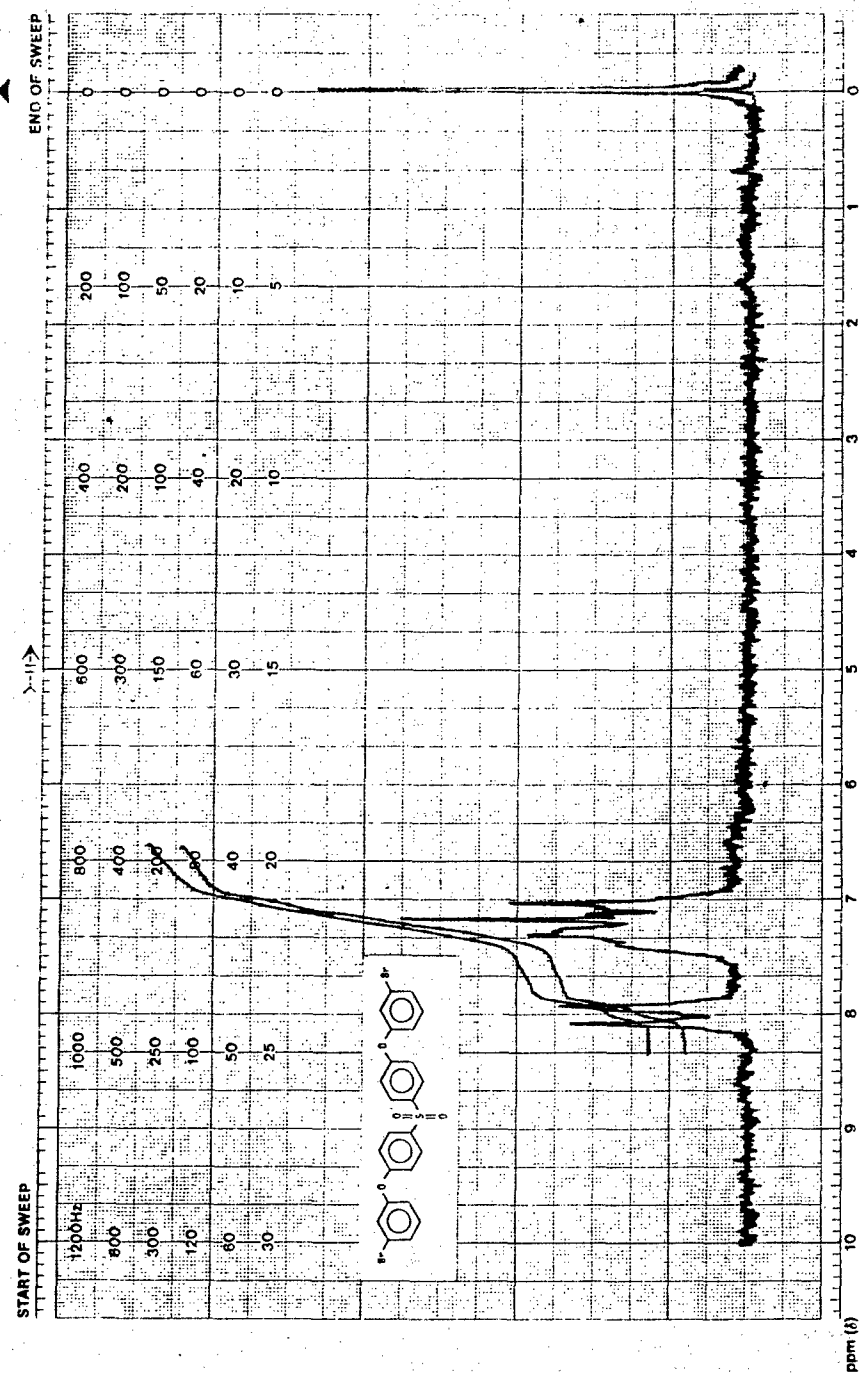FIGURE 4. Infrared Spectrum of BPDS.

28

FIGURE 5. ^{1}H NMR Spectrum of BPDS.

29

REFERENCES

1. For a recent comprehensive review see: P. M. Hergenrother, J. Macromol. Sci. Rev. Macromol. Chem., C 19 (1), 11 (1980).

2. C. E. Browning, Polym. Eng. and Sci., 18, No. 1, 16 (1978), and references therein.

3. G. A. Loughran and F. E. Arnold, AFWAL-TR-80-4011, (1980); ibid., Polym. Preprints, 21 (1), 199 (1980).

4. J. J. Harrison and C. M. Selwitz, AFML-TR-79-4183, December 1979.

5. E. T. Sabourin, AFWAL-TR-80-4151, October 1980.

6. A. A. Moroz and M. S. Shvartsberg, Russ. Chem. Revs., 43 (8), 679 (1974).

7. R. G. R. Bacon and O. J. Stewart, J. Chem. Soc., 4953 (1965).

8. F. L. Hedberg, M. R. Unroe, P. M. Lindley, M. E. Hunsaker, and W. A. Feld, Polymer Preprints, 24 (1), (1983); F. L. Hedberg, M. R. Unroe, P. M. Lindley, and M. E. Hunsaker, AFWAL-TR-85-4041.